

Effect of Functionality Levels and Compatibility of Polycarbonate Blends with Maleic Anhydride Grafted ABS

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ABSTRACT: ABS was melt grafted with maleic anhydride at three different levels of 1, 2, and 3 wt %. These three different modified ABSs were melt blended with polycarbonate using a single-screw extruder to choose a suitable maleic anhydride grafting level on ABS for better performance. For the compatibility study, binary blends of polycarbonate with ABS and maleic anhydride-grafted ABS were prepared over the entire range of compositions. Compatibility of these blends was studied using a Dynamic Mechanical Analyzer and by Differential Scanning Calorimetry. Both techniques suggest more partial compatibility for modified blend systems. In addition to this, DSC thermograms show multiple peaks between the transition points of ABS fractions and polycarbonate fractions for the polycarbonate/maleic anhydride-grafted ABS blends. These multiple peaks are characteristic of better partial compatibility with fine microstructure. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2102–2110, 1999

Key words: reactive blending; compatibility; morphology; characterization and mechanical properties

INTRODUCTION

Blending is one of the commonly practiced methods to extend application frontiers for polymeric materials. Polycarbonate/ABS blends are generally immiscible, but their commercial success is due to partial miscibility at specific internal compositions of ABS. There are many techniques employed to develop better morphology or stable dispersion. Reactive compatibilization is currently popular in the commercial polymer blend/alloy field. For example, stable and fine dispersions of a polyamide/polycarbonate blend system have been reported¹ to be made by the addition of a maleic

anhydride-grafted styrene–ethylene–butadiene–styrene block copolymer (SEBS-*graft*-MA). In recent times the reactive blending technique has been popularized, at least at the researchers' level. A recent example in the latter case is a maleic anhydride-grafted ABS addition to polyethylene terephthalate.²

Among engineering thermoplastics, amorphous polycarbonate is one of the most important polymers, distinguished by its versatile combination of good mechanical, thermal, and optical properties. Its limitations are high notch sensitivity, high melt viscosity, and poor chemical resistance. These are the properties that need to be improved to extend its engineering applications. These improvements are made by blending with ABS for commercial use. ABS was chosen to toughen the PC, based on prior information available in the literature regarding the capability of maleic anhydride grafted onto ABS and partial

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miscibility of these binary blend systems so that a better compatible blend can be made through the reactive blending method.^{2,3} Several articles are reported on toughening of various thermoplastics with maleic anhydride-functionalized thermoplastic elastomers.^{2,4,5} Cecere et al.⁴ have demonstrated the occurrence of an esterification reaction between maleic anhydride functionality on EPR-*g*-MA with a hydroxyl group of PBT. A similar reaction in the present system would occur during melt blending between anhydride functionality and the terminal hydroxyl group of polycarbonate. This results in compatibilization and stabilization of fine morphology. The morphology and mechanical performance of the resultant blends are influenced by the level of functionality.⁶

The mechanical properties of the materials, which are of relevance as they are deformed under periodic forces, are the storage modulus (E'), loss modulus (E''), and mechanical damping or internal friction (loss tangent, $\tan \delta$). The investigations of the moduli and internal friction over a wide range of temperatures and frequencies have proven to be very useful in studying the structure of polymers and the variation of properties in relation to performance.⁷ The dynamic parameters have been used to determine the glass transition temperature (T_g) of polymers. The largest loss peak is generally the α -peak, associated with the T_g , which occurs in the amorphous region of the polymer. High mechanical damping or internal friction is essential to decrease the effect of undesirable vibrations. The storage modulus indicates the inherent stiffness of the material under dynamic loading conditions. This value is related to the Young's modulus of polymers. The maximum heat dissipation per unit deformation occurs at the temperature where the loss modulus is maximum.

Differential scanning calorimetry (DSC) is a technique that measures the quantity of energy absorbed or evolved by a sample as it undergoes some transition (e.g., T_g , melting point, crystallization, curing, etc.) with a constant heating rate or constant temperature, and this difference in energy or difference in temperature is measured and plotted as a function of temperature or time.

The objectives of the present work are to identify a suitable level of functionality and improvement of processibility and notch-sensitive resistance of PC while retaining other mechanical properties through the latest technique-reactive blending. Morphological and compatibility fea-

tures are also examined to make the study more comprehensive.

EXPERIMENTAL

Polycarbonate (Lexan ML 3403) and an Acrylonitrile-Butadiene-Styrene terpolymer (ABS) (ABSOLAC SP 200) were procured respectively from GE Plastics India Ltd., and Bayer ABS Ltd., Vadodara, India. Maleic anhydride and benzoyl peroxide (BPO) were procured respectively from Loba Chemie, Mumbai, India, and BDH Chemicals Ltd, UK.

Initially, ABS with MA at three different wt % of MA, 1, 2, and 3 were dry blended respectively with 0.1, 0.2, and 0.3 wt % BPO as the initiator. The dry-blended materials were grafted in the temperature range of 190–200°C using a single-screw extruder with a mixing head. The extruded strands were quenched in cold water and pelletized. The granules were dried at 80°C for 2 days to remove unreacted maleic anhydride.^{8,9}

Blend compositions of 1, 2, and 3 wt % MA-grafted ABS at 35 wt % were prepared with 65 wt % PC; these blends were coded respectively as 1MP65, 2MP65, and 3MP65. PC/ABS blends were also prepared at similar 65 wt % PC level and coded as P65. The melt blending was done in the temperature range of 220–240°C using a single-screw extruder with a special mixing head. These series of blends were made to choose the suitable wt % MA grafting required for the detailed study. The extruded pellets of these blends were vacuum dried at 90°C for 8 h and injection molded to study the mechanical properties.

Tensile tests were carried out on a Zwick 1465 universal testing machine at room temperature following the procedure of ASTM D638. Injection-molded dumb bell-shaped specimens of dimensions $14 \times 1.5 \times 0.15$ cm were used. A crosshead speed of 0.5 cm/min was used for tensile properties measurement. Flexural properties also were measured using the same Zwick 1465 universal testing machine at room temperature following the procedure described in ASTM D790. Injection-molded specimens of dimensions $12 \times 1.4 \times 0.5$ cm were used for this study. A crosshead speed of 0.2 cm/min was used in all measurements.

Notched Izod impact strength was measured using a Frank impact tester at room temperature following the procedure described in ASTM D256. All the specimens had the dimensions of $6.2 \times 1.4 \times 0.5$ cm, with a notch radius of 0.025 cm. Phase

morphology has been characterized using a JEOL (JSM 5300) Scanning Electron Microscope (SEM). Scanning electron micrographs for notched Izod impact fractured samples of all the blends were made to determine ductile/brittle characteristics.

After completing the trial study at these three different MA wt % grafted levels of ABS (MABS) with PC blends, for compatibility study, 2 wt % MA-grafted ABS was used for reasons given later. The following blend compositions were made for a compatibility study.

Polycarbonate was melt blended with ABS in a wide range of compositions viz. 25, 35, 50, 65, 75, and 90 wt % levels. These compositions are coded respectively as P25, P35, P50, P65, P75, and P90. The blends of PC with MABS at similar compositions are coded as MP25, MP35, MP50, MP65, MP75, and MP90. Melt blending was carried out at different temperatures ranging from 210–240°C, depending on the composition; and the extrudate obtained had a smooth surface.

Dynamic mechanical properties of the blends were studied in a Rheovibron viscoelastometer Model-DDVII, a device to measure dynamic viscoelasticity and temperature performance of polymers. The blend materials were hot pressed at the melt temperature using a compression-molding machine, and then the mold assembly was quenched in cold water. Compression molded specimens of dimensions 50 × 5 × 0.5 mm were used for this purpose. Tests were carried out from 25 to 180°C at a heating rate of 2°C/min and a frequency of 11 Hz. DSC analysis was performed on a Du Pont DSC apparatus in a nitrogen atmosphere. The fusion thermogram was obtained by heating around 7 mg of samples from 30 to 170°C, at a heating rate of 5°C/min.

FTIR has become a powerful tool to study polymer functionalization and deterioration during melt blending in polymer blends. FTIR analysis was done for ABS, 1, 2, and 3% maleic anhydride grafted ABS, PC, and selective blends (P50 and MP50). The compression-molded thin specimens were used for the FTIR study.

RESULTS AND DISCUSSION

The initial part of this study was to choose optimum maleic anhydride content and then compatibility. I.R. characterization was carried out for the blend materials. The results are discussed in detail.

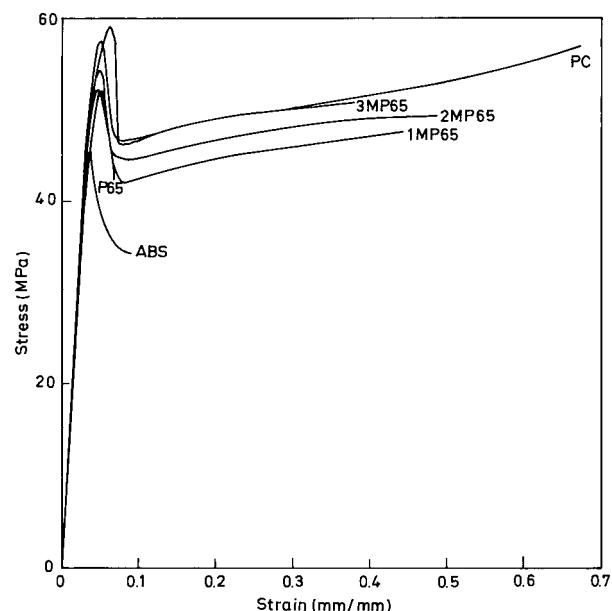


Figure 1 Stress–strain plots for feedstocks and PC/MABS blends using different maleic anhydride grafting level.

Effect of Functionality on Mechanical Performance

As the published reports^{2,4} reveal that 1 or 2 wt % MA grafting is sufficient to improve the performance by the reactive blending technique, 1, 2, and 3 wt % MA levels were grafted on ABS to choose one out of these three levels. Initially, the effects of different wt % MA-grafted ABS on the mechanical performance of PC/MABS blends were studied and compared with the results of physical blends of PC/ABS at a specific composition (65 wt % PC level), which is comparable with that of commercial PC/ABS blend composition.^{10,11} Mechanical properties of PC and ABS were also obtained and summarized with these results.

Tensile stress–strain plots of the above-mentioned blends and the feedstocks are given in Figure 1. It can be clearly observed that the feedstocks behave quite differently from the blends. PC shows cold drawing characteristics (plastic part) after yielding, whereas ABS shows necking characteristics with a small plastic portion. The physical blend P65 failed at a much lower strain, characteristic of semi-brittle material. This unexpected trend is due to physico-chemical changes among blend components during melt blending. This aspect is dealt with in detail later. The stress–strain curves for 1MP65, 2MP65, and 3MP65 blends show cold drawing characteristics

Table I Summarized Test Results of PC/MABS Blends at Different Maleic Anhydride Wt % Level

Blend Materials	Tensile Strength (MPa)	Tensile Break Strain (%)	Flexural Strength (MPa)	Notched Izod Impact Strength (J/m)
PC	59.13	67.22	92.47	126.4
1MP65	52.23	43.73	81.52	715.6
2MP65	54.43	51.23	83.11	745.1
3MP65	57.52	38.07	84.16	748.7
P65	52.42	6.92	52.75	52.7
ABS	45.29	10.23	64.66	320.3

very similar to that of PC. The break strain value for 2MP65 is the highest among these three modified blends. The slightly lower break strain in the case of 1MP65 may be attributed to a lower compatibilization effect due to a low wt % of the maleic anhydride-graft content. The lower break strain value of 3MP65 may be due to the deterioration of ABS because of the high percentage of peroxide used during melt grafting.

Apart from the tensile tests, flexural and notched Izod impact tests were also conducted on these blend materials, and the results are summarized in Table I. Tensile strength of the modified blends increases as the wt % of MA grafting level increases. Flexural strength values of modified blends do not show much variation with varying the wt % of MA. The notched Izod impact strength of 1MP65 is slightly lower than that of 2MP65, but those of 2MP65 and 3MP65 are almost same. As the present objective is to improve the notch sensitive resistance of PC, it is appropriate to consider notched impact property to choose a maleic anhydride grafting level to study the behavior of reactive blending of PC/MABS blends and compare these with physical blends of PC/ABS. SEM micrographs of fractured surfaces of these modified blends are given in Figure 2. The plastic deformation of the fractured surface increases as the wt % of the MA graft content increases. The microstructure of 2MP65 is fine compared to that of 1MP65. Although the plastic deformation of 3MP65 is the highest, the impact strength is nearly the same as that of 2MP65. The lower maleic anhydride grafting level is preferable, because maleic anhydride is volatile and toxic, and during melt grafting considerable vapors are evolved. This vapor is also an eye and nasal irritant, and hence, a higher percentage of grafting is not preferable. Hence, a 2 wt % grafting level is the optimum to study the performance

of reactive blended PC/MABS blends. The notched impact strength value for P65 is very low compared to that of MP65 or even PC. This deterioration is due to poor interfacial interaction, and this might be due to melt deterioration of the PC phase by the catalyst or surfactant remnants present in the ABS.¹² Hereafter, the 2MABS and 2MP65 will be referred to, respectively, as MABS and MP65.

FTIR Spectroscopic Analysis

FTIR is a well-known tool to identify the chemical groups in a chemical compound. In polymer science, it has been used to identify a particular group, chemical structural changes—particularly in melt-blended polymer blends—and physico-chemical interactions in the resultant blends. The appearance of a new peak for a blend that is not found in blend components is a consequence of physico-chemical changes during melt blending.

IR spectra of maleic anhydride grafted ABS, 1MABS, 2MABS, and 3MABS are given in Figure 3. The appearance of sharp peaks at 1788 cm^{-1} and 1716 cm^{-1} (carbonyl, CO stretching), which are absent in ABS's spectrum (Fig. 4), is ample evidence about grafted maleic anhydride functionality. The increase in intensity of peak at 920 cm^{-1} (CO bending) compared to that of ABS is also evidence of MA grafting on ABS.

The occurrence of degradation in the PC/ABS blend was proven by IR analysis.¹² IR spectra of PC, ABS, and blends are given in Figure 4. A strong peak appears at 3532 cm^{-1} for the unmodified blend (P50), but it is less marked for ABS, PC, and the modified blend (MP50). These results imply that the PC of the PC/ABS blend is degraded during melt blending by the catalyst or surfactant remnants present in ABS.

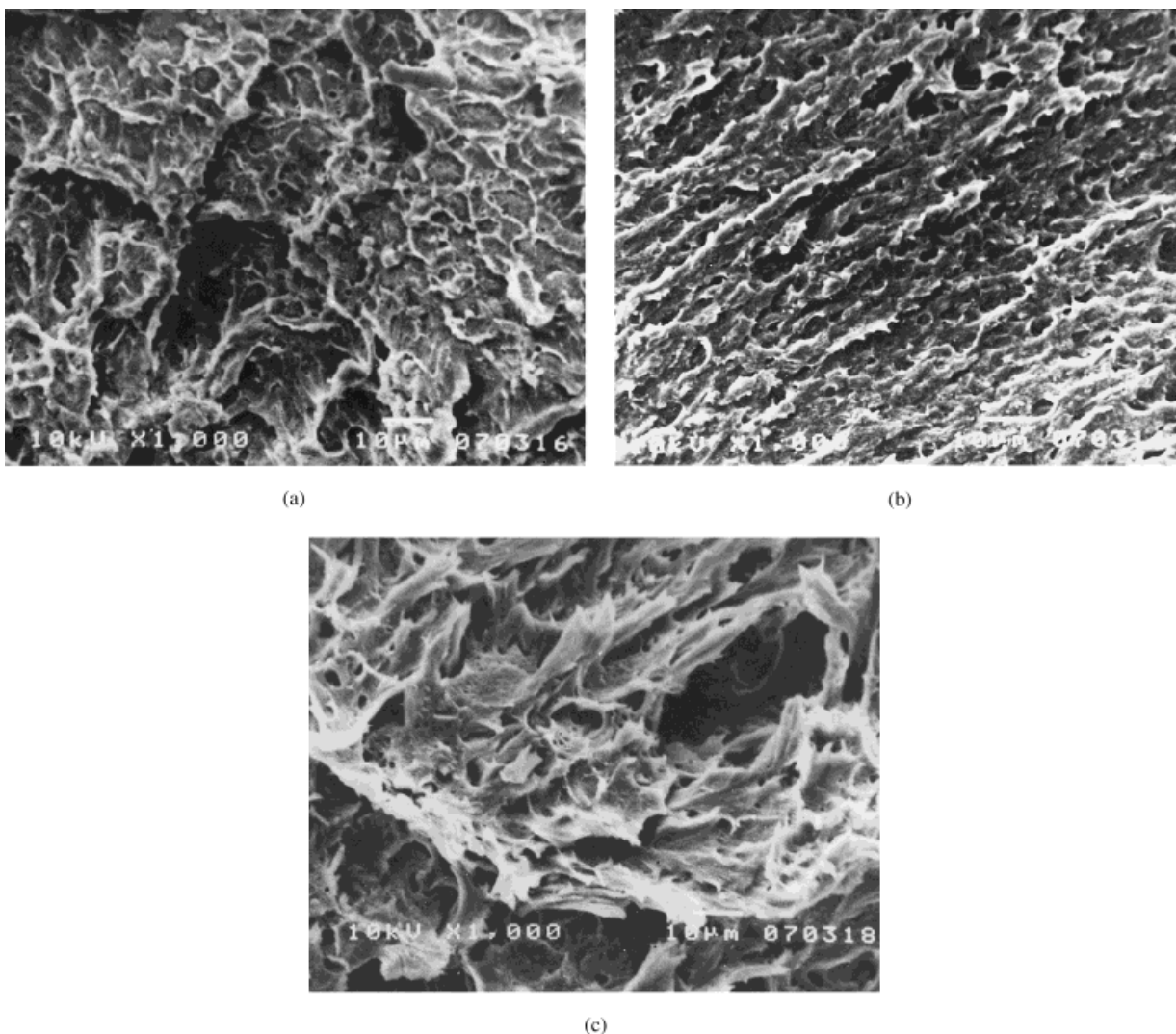


Figure 2 SEM micrographs of the fractured surface of PC/MABS at different anhydride grafting levels (a) 1MP65, (b) 2MP65, and (c) 3MP65.

DMA Analysis

Miscibility of polymer blends can be determined from the viscoelastic data obtained by dynamic mechanical analysis (DMA). DMA measures the response of a polymer to periodic and fluctuating loads and is extremely sensitive to all types of transitions. Polymeric materials under service conditions, such as parts in engineering applications, are frequently subjected to dynamic load-elongation field. Dynamic mechanical properties such as storage modulus (E'), loss modulus (E''), and damping factor ($\tan \delta$) are of great importance in determining and understanding the behavior of materials under these conditions. In this section, dynamic mechanical

behavior of the physical blends (PC/ABS), as well as reactive blended blends (PC/MABS), is analyzed.

The viscoelastic properties of polymers depend on the thermal history of the samples, because it influences their morphology. The $\tan \delta$ vs. temperature plots for unmodified blends are given in Figure 5, and those for modified blends are given in Figure 6. Characteristic damping peaks are observed for PC and ABS, and these are, respectively, at 151 and 110°C. These damping peaks are their respective glass transition temperatures. The transition in ABS is due to the randomness of SAN copolymer; it should be assigned to the main transition of the

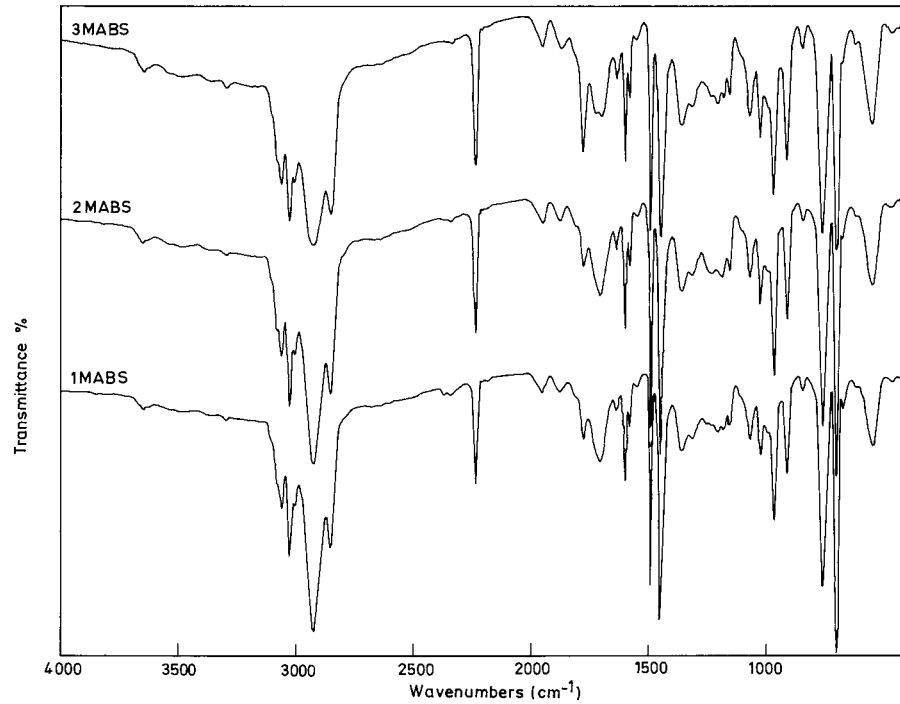


Figure 3 FTIR spectra for different wt % maleic anhydride-grafted ABS.

styrene-acrylonitrile part of ABS. The primary relaxation of the polymer corresponding to the T_g results from the initiation of the micro-

Brownian motion of the amorphous chain. The MABS (Fig. 6) also shows a similar peak at 110°C to that of ABS.

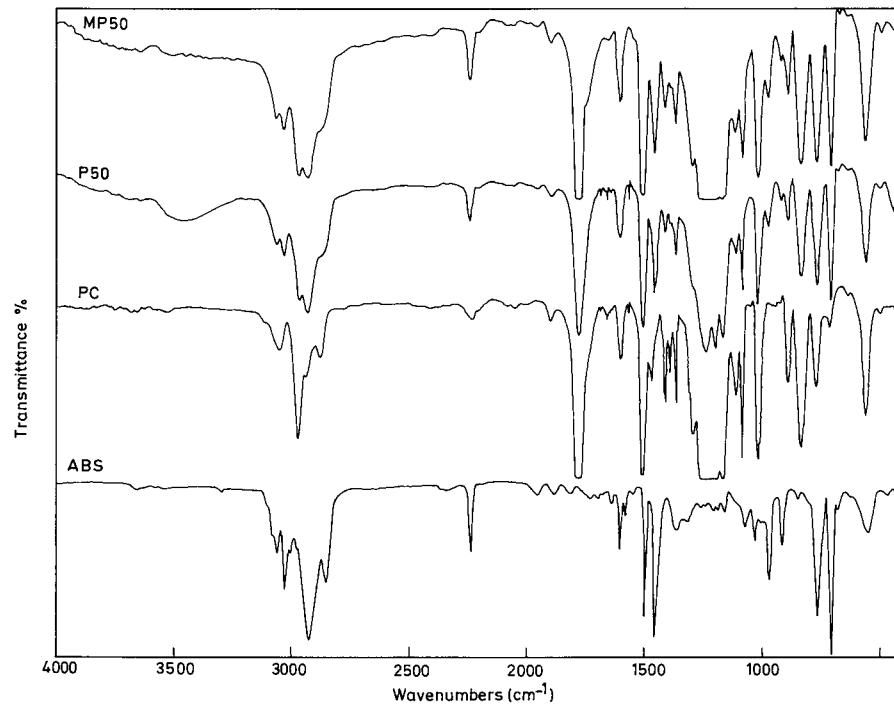


Figure 4 FTIR spectra for PC, ABS, and selective blends (P50 and MP50).

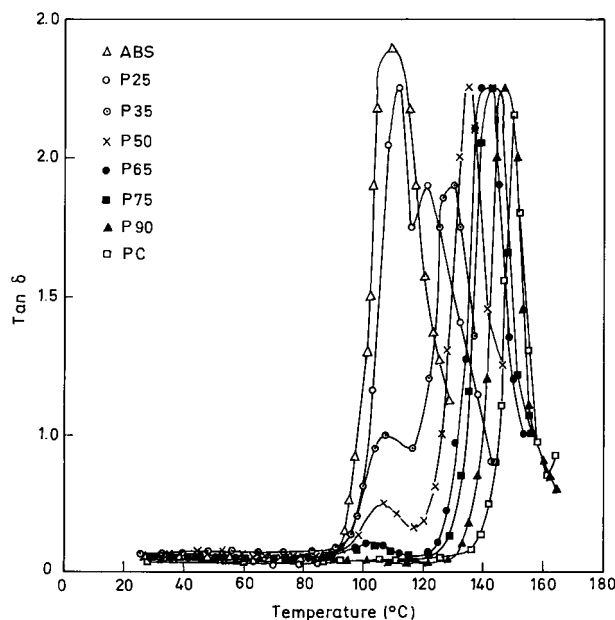


Figure 5 Tan δ vs. temperature plots for PC/ABS blends.

The tan δ relaxation peaks for unmodified as well as modified blends are more or less the same. All the blends show two transition peaks in the experimental regime. As the wt % PC decreases, the transition temperature (tan δ peak) corresponding to PC decreases for both blend systems. This decrease is consistent with partial miscibility, and may be due to reduction of molecular weight of PC during melt blending by catalyst or surfactant remnants present in ABS.¹² The transition peaks in both these blend systems, corresponding to ABS's SAN segment, show a minor decrease from 110 to 106°C as the composition is varied. This trend is not consistent with the data obtained with DSC. This discrepancy may be attributed to the differences in the methods of sample preparation for DSC and DMA. Kim and Burns¹³ found that decrease of T_g of the PC phase in the PC/ABS blends is more than that in the PC/SAN blends. They also suggested that the solubility of ABS is more in PC than that of PC in ABS. As the low molecular weight fraction of ABS enters into the PC, it results in plasticization, and a reduction in T_g of PC is observed as the composition is varied. Horiuchi et al.¹ studied DMA of PA-6/PC blends. They revealed that the T_g s of polyamide 6 (PA-6) and PC phases in the blends were slightly lower than those of the respective pure polymers when the compatibilizer was added. They also found that incorporation of sty-

rene-ethylene-butadiene-styrene block copolymer graft-maleic anhydride (SEBS-*g*-MA) in that blend system did not affect T_g s of either phase. This indicates that chemical reactions occur between PA-6 and PC during melt blending, which produce low molecular species of PC regardless of the incorporation of SEBS-*g*-MA, and that SEBS-*g*-MA on the domain boundary is not miscible enough to reside within the PC domains. A similar explanation may be applicable to the present unmodified and modified PC/ABS blend systems. Although fine dispersion of the dispersed phase in the PC/MABS blends has been proven by SEM micrographs,¹⁴ this does not influence the T_g of the blend components. The mechanical performance of the PC/MABS blends was much superior to the PC/ABS blends.¹⁵

The storage modulus (E') vs. temperature curves of unmodified and modified blends are supportive evidence for partial miscibility.¹⁶ The dynamic modulus relates the inherent stiffness of the material under dynamic loading conditions. The initial E' values of the blends were near those of the blend components. The E' values for feedstocks showed only one transition level at their respective T_g s, whereas all the blends showed two transition levels, which are related to blend components. The loss modulus (E'') vs. temperature curves of unmodified and modified blends are also supportive evidence for partial

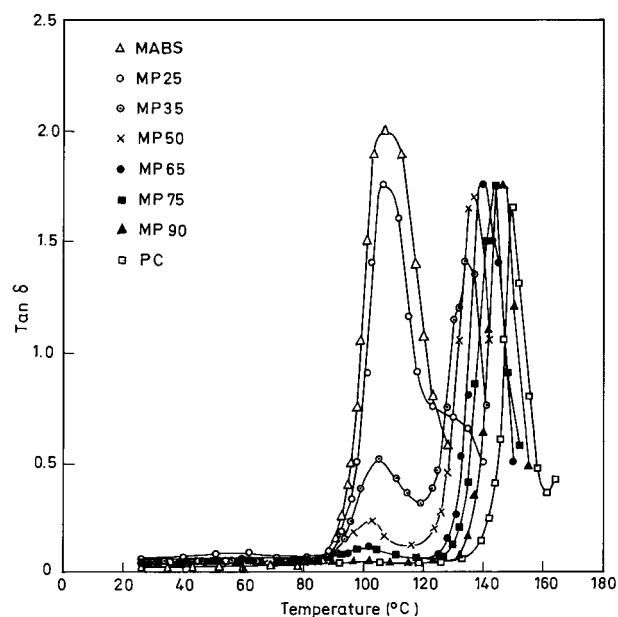


Figure 6 Tan δ vs. temperature plots for PC/MABS blends.

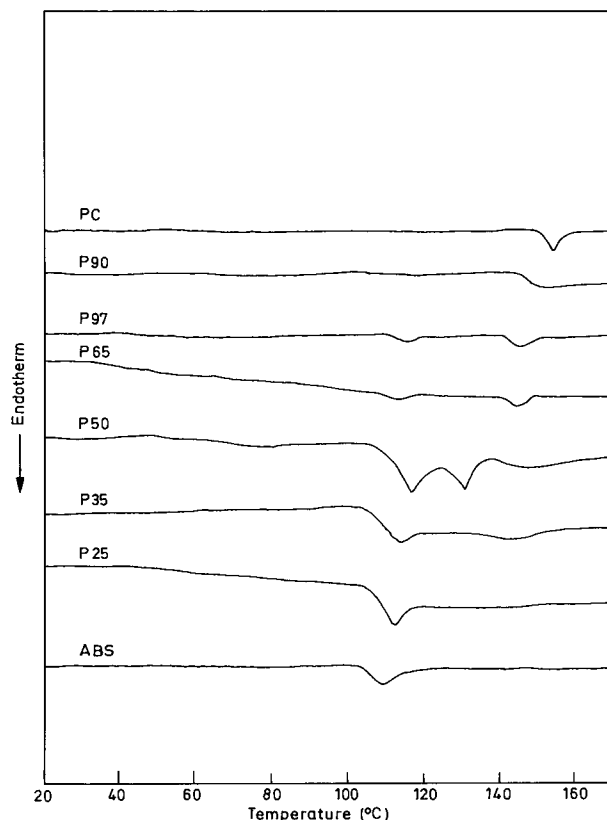


Figure 7 DSC thermograms for PC/ABS blends.

miscibility. The loss modulus is sensitive to many kinds of molecular motions, transitions, relaxation processes, structural heterogeneity, and the morphology of multiphase systems.

DSC Analysis

In polymer blends, the compatibility is also determined using this technique. A clear shift in the glass transition temperature, by changing the blend ratio, can be seen in the DSC thermograms shown in Figures 7 and 8, respectively for unmodified and modified blends. For the temperature region investigated, the parent polymers, PC and ABS, show single transitions only, and the blends show two transitions. The glass transition temperature for virgin materials is 153°C for polycarbonate and 110°C for ABS. It is between these two temperatures for the blends. A shift in transition temperatures is a well-known phenomenon found in the partial miscible blend systems.¹⁷ The phases interact with each other at their interfaces so that the transition is affected, the net result being a shift in observed transition temperatures.

It is interesting to note that the shift in temperature is observed for both the blend components at all compositions. As expected, the transition shift for the PC phase is decreased in temperature, compared to that of virgin PC, and the transition shift for ABS phase is increased in temperature, compared to that of virgin ABS. In some compositions there are no two clear transition peaks in between those of PC and MABS fractions for modified blends, MP50 and MP65. This aspect is characteristic of that of compatibilized blends with fine microstructure¹⁸ and more compatibility. Therefore, the DSC results suggest that both the blend systems are partially miscible and PC/MABS blends are more partially miscible.

CONCLUSIONS

1. The optimum maleic anhydride grafting level was found to be 2 wt % on ABS for reactive toughening with polycarbonate.
2. PC/MABS blends showed tremendous improvement in notched impact strength, whereas the PC/ABS blends showed much

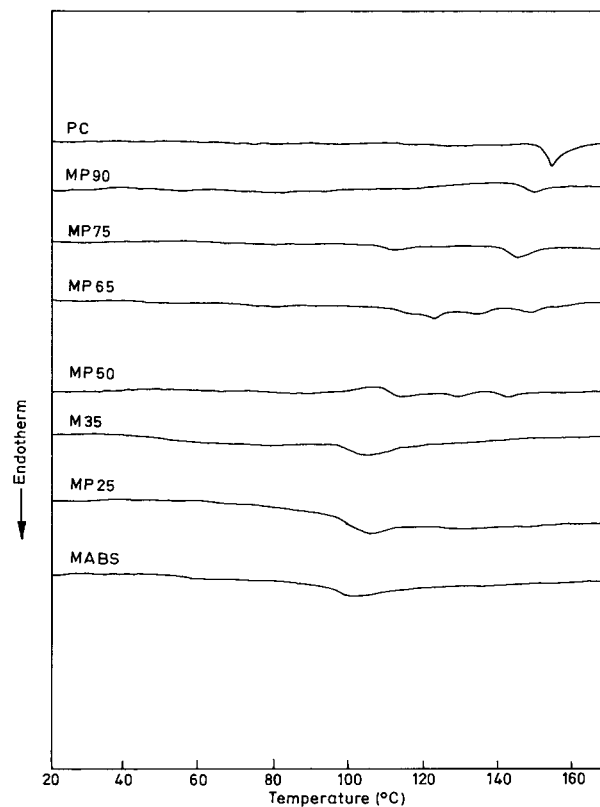


Figure 8 DSC thermograms for PC/MABS blends.

low values compared to that of polycarbonate.

3. DMA and DSC studies provide further evidence for the partial compatibility of these blends. The decrease in the shift of the T_g of the PC components and the increase in the shift of the T_g of the ABS/MABS components in these blend systems are ample evidence for their partial compatibility. The observed multiple DSC transition peaks in between those of ABS and PC fractions for modified blends are evidence for more partial compatibility with fine dispersion.
4. FTIR spectra confirm the grafting of MA on ABS and also give evidence for melt degradation in the case of unmodified blends.

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